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Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood

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HIGHLIGHTS

- ▶ Treating biomass below 300 °C does not have a major effect on product yields.
- ▶ Guiacyl (G) units decrease when the biomass is heated over 300 °C.
- ▶ The yield of levoglucosan reduces when the biomass was heated over 260 °C.
- ▶ The yield of water increases in the whole range of temperature studied.

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ABSTRACT

This paper investigates the effect of thermal pretreatment temperatures between 200 and 370 °C on the yield and composition of products (bio-charm gasm water and organics) obtained when Douglas-fir wood was subsequently pyrolyzed in an auger reactor at 500 °C. The yield of products was reported for the pretreatment and pyrolysis steps separately, and for the two steps added. The maximum yield of bio-oils achieved without pretreatment was close to 59 mass%. A decrease in total liquid yield was observed when the biomass was pretreated at 300 °C. At higher temperatures, the yields of Douglas-fir primary degradation products (lignin oligomers, anhydrosugars and alkylated and methoxylated phenols) decreased. The overall water yield increased gradually to 14 mass% at a pretreatment temperature of 290 °C. The yield of lignin oligomers also decreased as the pretreatment temperature increased. A drastic reduction in the yield of methoxylated phenols derived from guaiacyl (G) was observed when the biomass was pretreated at temperatures over 300 °C. This drastic reduction in the yield of methoxylated lignin derivatives can be explained by the formation of liquid intermediates that facilitate the formation of ionic species, enhancing dehydration reactions leading to the production of o-quinone methide intermediates critical for bio-char formation.

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1. Introduction

The production of transportation fuels derived from forest and agriculture wastes is a promising alternative to reduce our overdependence on imported oil and to reduce the green house gases emissions associated with the combustion of fossil fuels. In 2007, the United States Energy Independence and Security Act (EISA) urged the industry to produce 9 billion gallons of renewable fuel by 2008 and an additional 36 billion gallons annually by 2022 to replace 20% of the transportation fuels consumed [1]. Meanwhile, the European community also established a target of 10% renewable fuels by 2020 [2]. To produce such quantities, new technologies need to be developed to convert lignocellulosic materials into transportation fuels. Among the technologies studied, pyrolysis is very promising because it allows the conversion of between 60 and 75 mass% of lignocellulosic materials into a crude bio-oil [3,4] that can be further refined via hydrotreatment to produce transportation fuels [5].

Improving the quality of bio-oils is a major research goal for the biomass thermo-chemical community [6–13]. The properties of the feedstock [14], pyrolysis conditions [8,9], and particle size [13,15] are the three main factors affecting bio-oil quality. Thermal pretreatment in the range of temperature between 200 and 300 °C in the absence of oxygen (torrefaction) could modify some of these parameters and affect bio-oil yield and quality [16,17]. When biomass is heated between 200 and 300 °C hemicellulose is typically thermally degraded and the weak glycosidic bonds of amorphous cellulose break resulting in the formation of cellulose with between 150 and 400 glucose units [18,19]. This cellulose with constant degree of polymerization is often called “activated

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cellulose", and is considered by some authors an intermediate product of pyrolysis reactions [18,20]. In this temperature range (200–300 °C), biomass weight loss is mainly due to dehydration, decarboxylation and deacetylation of xylan-containing hemicellulose polymers [21].

Thermal pretreatment at temperatures between 275 and 300 °C could reduce grinding energy [22,23]. This is critical for fast pyrolysis given the sensitivity of bio-oil yield and composition to biomass particle size [13,15]. High yields of bio-oil can only be achieved if biomass particles with diameters below 2 mm are used.

Despite the potential of thermal pretreatment to reduce grinding energy, there are few reports discussing its effect on the yield and quality of pyrolysis products [24–26]. The effect of thermal pretreatment at a temperature of 280 °C on the yield of products obtained from an auger pyrolysis and fluidized bed reactor at 350 °C, using beech, poplar, spruce and straw, was studied by De Wild et al. [25]. The authors concluded that staged pyrolysis could be a promising route to appreciate lignocellulosic materials. The main goal of this paper is to evaluate the effect of thermal pretreatment on the yield and composition of bio-oils obtained from Douglas-fir wood in an auger pyrolysis reactor in the range of temperature between 200 and 370 °C.

2. Experimental methods

2.1. Biomass preparation

The Douglas-fir wood studied was grown in Port Angeles, Washington and was kindly donated by Herman Brothers Logging & Construction, Incorporated (Port Angeles, WA). The samples were stored in a refrigerator at 4 °C and ground by a pioneer mill (Model number 400 HD, serial number 2404, Bliss Industries, Inc.) to a particle size below than 2 mm [27].

2.2. Thermal pretreatment and pyrolysis

Between 500 and 600 g of Douglas-fir wood samples were thermally pretreated in every experiment with an auger reactor [27]. Briefly, the dried biomass in the hopper was fed with a volumetric feeder (Barbender Technologies) into the auger reactor at a feed rate of 10–12 g/min. A stainless-steel tube 58.5 cm length and 10 cm diameter was heated by a Lindberg/Blue M (model HTF55322A) furnace. The biomass was pushed through the hot zone of the reactor with an auger screw driven by a 1 hp variable speed motor. Nitrogen at 10 L/min was used as the carrier gas and the auger speed was set at 5 rpm for the torrefaction process, corresponding to a residence time of 72 s. The thermally pretreated biomass obtained between 270 and 370 °C was collected in a pot. The pretreated biomass was left to cool in the pot and was then pyrolyzed in the same auger reactor at 500 °C. The estimated residence time of the vapors inside the pyrolysis reactor was approximately 8 s. All the pyrolysis experiments were conducted at auger speeds of 13 rpm which corresponds to a biomass residence time of approximately 30 s. For both the thermal pretreatment and the pyrolysis tests the temperature on the external wall was set and recorded as well as the temperature of the biomass bed at the exit of the heating zone and at the entrance into the collection pot. The vapors resulting from the pretreatment and the pyrolysis steps were condensed in three condensation units as described elsewhere [27]. The pressure inside the reactor was kept under a very slight vacuum of −2 mm H_2O by sucking the pyrolytic vapors and the carrier gas through the condensers with a vacuum pump. The yield of liquid was determined by weighing the liquid collected in the traps, the vacuum pump and the condensers. The non-condensable gases were calculated by difference.

2.3. Pretreated biomass analyses

The contents of extractives, cellulose, lignin, and hemicelluloses in thermally pretreated Douglas-fir wood were measured following ASTM methods (ASTM D1105-96, D1106-96, E1758-01). The extractives were measured by soxhlet extraction using ethanol and toluene as solvents. The cellulose and hemicelluloses contents were calculated by the mono-sugar content after two step sulfuric acid hydrolysis and analysis in an ionic exchange chromatograph. Lignin content includes acid soluble and acid insoluble fraction. The acid soluble lignin was obtained by UV spectroscopy and the acid insoluble lignin was calculated as the solid residues left after acid hydrolysis.

2.4. Thermogravimetric analyses

The thermally pretreated samples were dried at 105 °C and analyzed thermogravimetrically in a Mettler-Toledo TGA/SDTA851 analyzer. Between 5 and 10 mg of the different samples were put into the pans and heated at 10 °C/min. The final temperature inside the furnace was 600 °C and the nitrogen carrier gas flow rate was 20 ml/min.

2.5. Bio-oil analysis

The chemical composition of the liquid collected during the thermal pretreatment and pyrolysis step was determined using the methods described below.

2.5.1. Water content

The water contents of thermal pretreatment and pyrolysis liquids were measured by Karl-Fisher Titration (Schott Titroline KF) using Hydranal Composite 5K as reagent (ASTM E203-08).

2.5.2. GC/FID and GC/MS

The content of methanol in the liquids collected was determined with a GC/FID (Shimadzu GC-2014 with AOC-5000 auto injector) equipped with a head space analyzer (oven temperature 85 °C) [27]. Briefly, the vapor in contact with the sample (250 μl) was injected into a 30 m × 0.25 mm ID column with a 0.25 μm film (HP-INNOW) using helium at 27.9 cm/s as the carrier gas. The GC/FID was operated in split mode (split ratio: 1:25), with an inlet and the FID at 180 °C and 210 °C respectively. The oven temperature of the GC was held at 45 °C for 1 min followed by heating at a rate of 5 °C/min until 70 °C (holding time at the final temperature: 2 min). The column was then heated to 200 °C (at a heating rate of 65 °C/min) and held at this temperature for 5 min to ensure the removal of all heavy molecules.

The content of selected volatile organic compounds heavier than water was measured with a GC/MS (Agilent 6890N). The instrument was calibrated with solutions of standard (selected) compounds at five different concentrations. Phenanthrene was the internal standard used to determine the response factor for each of the compounds analyzed in the conditions used in the GC/MS. Methanol solutions containing 5 mass% of oil sample and 0.2 mass% of phenanthrene were analyzed. All of the solutions were filtered (0.45 μm) to remove bio-char particles from the oil. Filtered solutions (1 μl) were injected into the inlet at 200 °C and working with a split ratio of 20:1. The vapors from the inlet were separated by capillary column (Agilent HP-5 MS, HP19091S-433) using helium as a carrier gas (1 mL/min). The column was held at 40 °C for 1 min, heated at 3 °C/min until 280 °C, and held for another 10 min at the final temperature. The mass spectrometer was operated with a transfer line temperature at 150 °C, an ion source temperature at 230 °C, and an electron impact ionisation (EI) at 70 eV. The mass of the fragments obtained was scanned from 28 to 400 (amu). Each of the peaks obtained was identified with the NIST/EPA/NIH mass spectral library (Version 2.0d, Fair Com Corporation).

2.5.3. Lignin-oligomers

The content of lignin oligomers in the liquids collected in the pretreatment and pyrolysis steps was determined by cold water precipitation following the method described elsewhere [8,9,30–32]. Briefly, approximately 2.5 g bio-oil was added drop wise with a syringe into a tree-neck round-bottom flask containing DI water (100 ml) that was stirred vigorously. The flask was immersed in ice to keep the water temperature close to 0 °C. The solid precipitated was separated by filtration with filter paper and washed with DI water (50 ml) until the color of the liquid became a completely clear yellow. The filtrates were stored in the refrigerator for hydrolysable sugars analysis. The remainder on the filter paper was washed with dichloromethane until the color of the filtrate became completely clear. The water insoluble/CH_2Cl_2 soluble fraction was recovered after the removal of the solvent with a rotary evaporator. This fraction is typically associated with the low molecular weight lignin oligomers [7–9,30–32]. The solid left on the filter will be referred to this paper as "water – CH_2Cl_2 insoluble pyrolytic lignin" or as "heavy lignin oligomers" [7–9,30–32].

2.5.4. Sugars

The content of hydrolysable sugars in the liquid collected in the thermal pretreatment and pyrolysis steps was determined by ion exchange chromatography (IEC) using a Dionex ICS-3000 with an AS 50 auto-sampler, GP 50 gradient pump, ED50 electrochemical detector, and a 30 m × 3 mm inner diameter column (CarboPac PA20). The filtrate from the determination of pyrolytic lignin (10 ml) was hydrolyzed at 130 °C with 2 ml sulfuric acid (H_2SO_4) at 0.5 M in a sealed glass vial for 4 h. The hydrolyzed solution (0.1 ml) was diluted with E-pure water 50 times and neutralized with sodium hydroxide (0.1 M). 10 µl of the neutralized sample prepared were then injected into the IEC to quantify the content of hydrolysable sugars. The mobile phase was deionized water and an aqueous sodium hydroxide solution at a flow of 0.5 mL/min. The column was maintained at 35 °C and the detector at a pH of 10.4. The characterization and quantification of all the sugars were performed based on the residence time and linear calibration curves of sugar standards (fructose, arbinose, galactose, glucose, mannose and xylose).

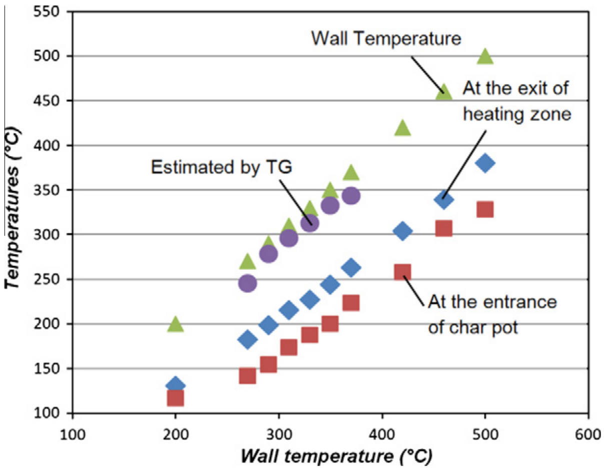

Fig. 1. Reactor wall temperature vs. estimated temperature of solid residues.

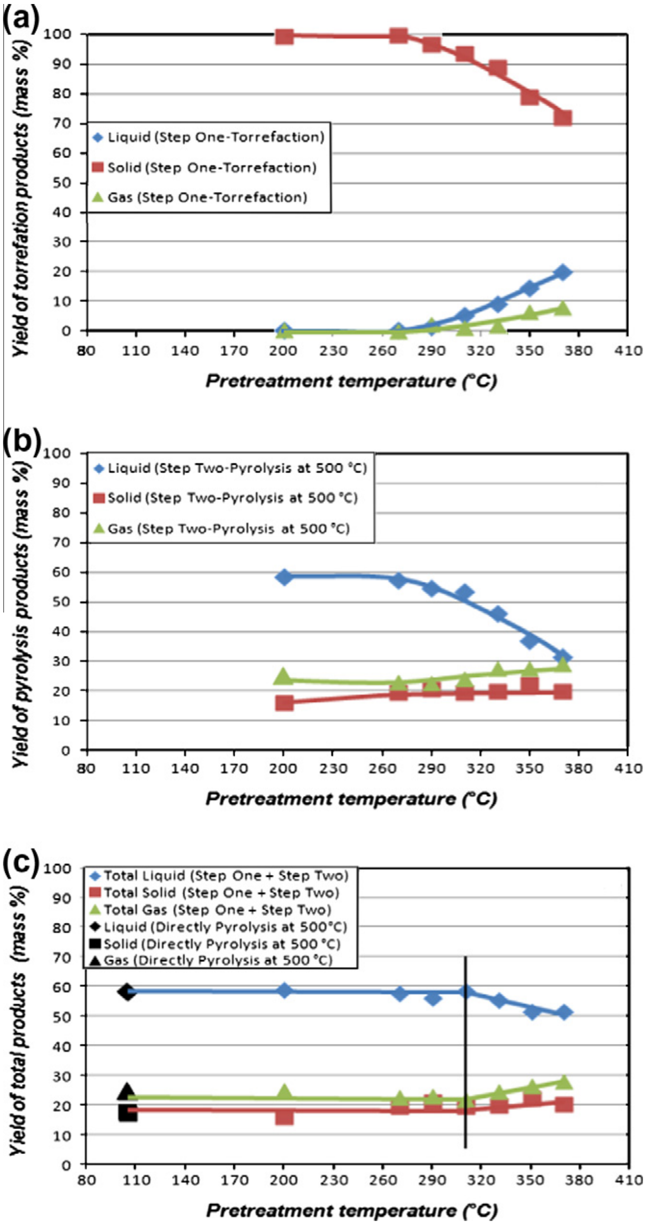

Fig. 2. Effect of pretreatment temperature on the yield of products obtained when the pretreated biomass is pyrolyzed at 500 °C. (a) Thermal pretreatment step (b) pyrolysis step and (c) yield of products when adding the pre-treatment and pyrolysis steps, with yields normalized per gram of dry initial biomass.

3. Results and discussions

3.1. Mass balances

One of the major challenges when describing the results obtained with an auger pyrolysis reactor is to assign an effective pyrolysis temperature and an "average" heating rate. According to the heat transfer theory in moving beds [28] the biomass particles will reach the wall temperature when they touch the reactor wall and then will transfer heat to the surrounding particles as it

Table 1
Biomass composition of different fractions obtained after pretreatment process (mass% on biomass dry basis).

Thermal pretreatment temperature (°C)	Extractives	Acid insoluble lignin (including ash)	Acid soluble lignin	Arabinose	Galactose	Mann/ xylose	Glucose
0	1.0 ± 0.1	26.6 ± 1.1	0.66 ± 0.09	0.91 ± 0.1	3.22 ± 0.02	15.0 ± 0.1	45.8 ± 0.9
200	1.3 ± 0.2	29.6 ± 1.5	0.63 ± 0.14	1.07 ± 0.1	2.55 ± 0.06	14.0 ± 0.7	41.4 ± 0.8
270	1.1 ± 0.2	26.6 ± 1.3	0.85 ± 0.1	0.70 ± 0.03	3.34 ± 0.22	14.1 ± 0.7	35.0 ± 1.3
290	1.1 ± 0.3	28.0 ± 1.9	0.68 ± 0.02	1.03 ± 0.07	2.64 ± 0.03	16.3 ± 0.7	46.8 ± 2.1
310	1.7 ± 0.2	27.8 ± 1.3	0.54 ± 0.18	0.60 ± 0.03	3.61 ± 0.11	12.2 ± 3.4	41.6 ± 1.2
330	1.7 ± 0.9	31.3 ± 4.4	0.63 ± 0.03	0.69 ± 0.19	3.45 ± 0.38	9.2 ± 2.9	37.9 ± 5.2
350	3.3 ± 0.9	34.5 ± 1.8	0.85 ± 0.002	0.23 ± 0.08	0	9.4 ± 0.3	41.5 ± 0.1
370	3.1 ± 0.6	41.7 ± 0.5	0.83 ± 0.02	0.31 ± 0.09	0	9.2 ± 1.2	42.0 ± 1.0

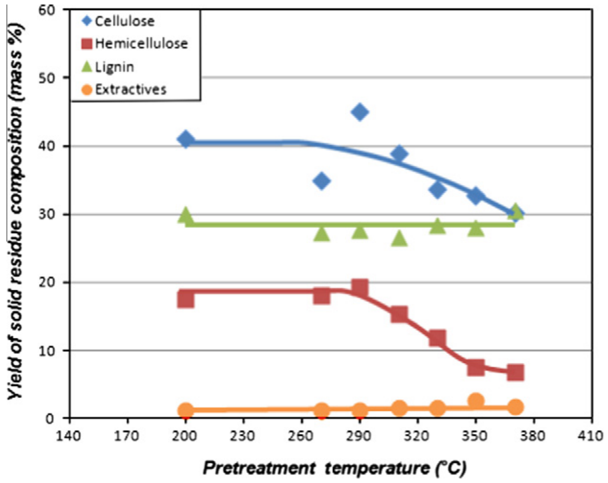

Fig. 3. Effect of pretreatment temperature on the composition of pretreated solid in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

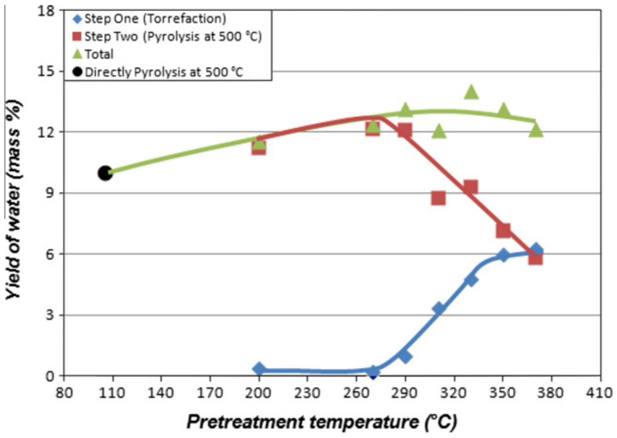

Fig. 5. Effect of pretreatment temperature on the yield of water in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

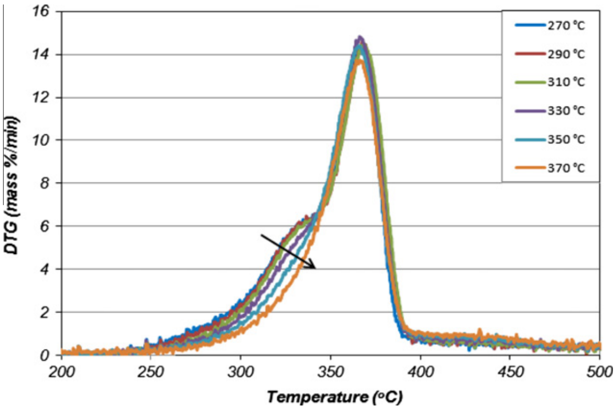

Fig. 4. DTG curves of biomasses pretreated at different temperatures with heating rate 10 °C/min.

moves away to the wall. Consequently the biomass particle is likely to be subjected to relatively large temperature gradients as it moves along the auger reactor. Because pyrolysis reactions at 500 °C are very fast, (according to Hoekstra et al. [29]), the total reaction times in kinetically controlled regime of less than 1 s, very high conversions could be achieved if the particle stays in contact with the wall less than 1 s even if the bulk temperature of the bed is relatively low. The complex heat and mass transfer of particles in the pyrolysis reactor makes the quantification of heating rate difficult as, the temperature–time history is complicated. Based on these considerations, De Wild et al. [25] estimated the effective temperature in an auger reactor as the temperature at which the weight losses obtained with a thermogravimetric analyzer equal the weight losses found in his auger reactor. Preliminary tests were conducted at different wall temperatures [27] and the weight losses obtained were used to estimate the effective pretreatment temperature using the thermogravimetric data obtained at 10 °C/min. Fig. 1 shows the relationship between the wall temperature, the effective pretreatment temperature estimated from the thermogravimetric analyses, and the temperature measured in the bed at the exit of the zone heated by the oven and at the entrance of the char pot. The temperature estimated by TG is very close to the wall temperature suggesting that in spite of the fact that the bed temperature is considerably lower conversions comparable to those expected for the wall temperature can still be achieved.

Fig. 2 shows the effect of pretreatment temperature on the yield of products (liquid, char and gas) obtained in the pretreatment step (Fig. 2a), during the pyrolysis of pretreated materials (Fig. 2b) and when the yields obtained in both steps were added (Fig. 2c). All the yields are expressed per gram of dry biomass before torrefaction (dry basis as received). The maximum yield of liquid was obtained with untreated biomass (59 mass%). This value is close to the yield reported for the same material when pyrolyzed in a fluidized bed reactor [33]. The total yield of liquid, liquid collected in the torrefaction step (Fig. 2a) plus liquid collected in the pyrolysis step (Fig. 2b), decreases to 50 mass% (see Fig. 2c) when the pretreatment temperature reaches 380 °C. Bio-char yield reaches 20 mass% when the

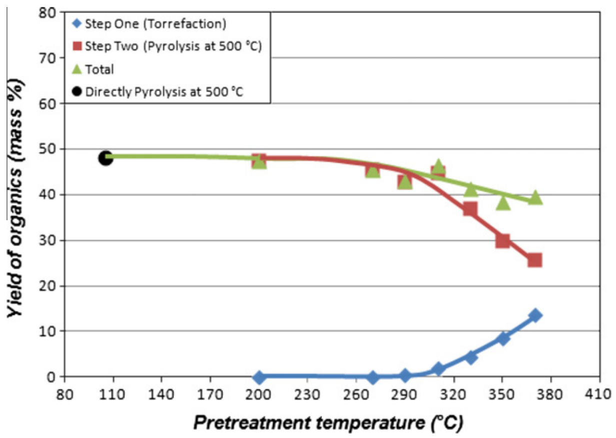

Fig. 6. Effect of pretreatment temperature on the yield of organics in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

pretreatment temperature increases to 380 °C. The total yield of gas increases from 22 mass% to 28 mass% as the pretreatment temperature increases from 300 °C to 380 °C. The overall yield of products does not change when the biomass was heated at temperatures below 300 °C. These results imply dehydration and cross-linking reactions at temperatures below 300 °C; however, these reactions are not significant enough to reduce the overall bio-oil yield of liquids when the pretreated biomass is heated at 500 °C. At temperatures over 300 °C the increase in gas yield can be explained by the formation of CO_2 and CO from the cross-liking and polymerization reactions. At temperatures over 400 °C the transglycosylation reactions, responsible for the formation of anhydrosugars, compete with cross-linking and polymerization reactions and a reduction in the production of CO_2 is typically observed [34].

3.2. Solid analysis

Table 1 shows the composition of the materials obtained at thermal pretreatment temperatures between 200 and 370 °C. It is worth noting the reduction in the concentration of arabinose, galactose and mannose/xylose and the increase in the content of extractives, acid insoluble lignin and glucose (mostly from cellulose) in the solid residue obtained in the thermal pretreatment step. The apparent increase in the concentration of extractives can be explained by the removal of hemicellulose and by the formation of a lignin soluble fraction derived from the cleavage of lignin weak ether bonds in the range of pretreatment temperature studied [37].

The sugars associated with the hemicelluloses (arabinose, galactose, mannose and xylose) show the most rapid decrease during pretreatment. Hemicellulose is a heterogeneous branched polysaccharide with a low degree of polymerization [35]. Because of its low degree of polymerization and amorphous structure, hemicellulose break downs easily at the thermal pretreatment temperatures studied [36].

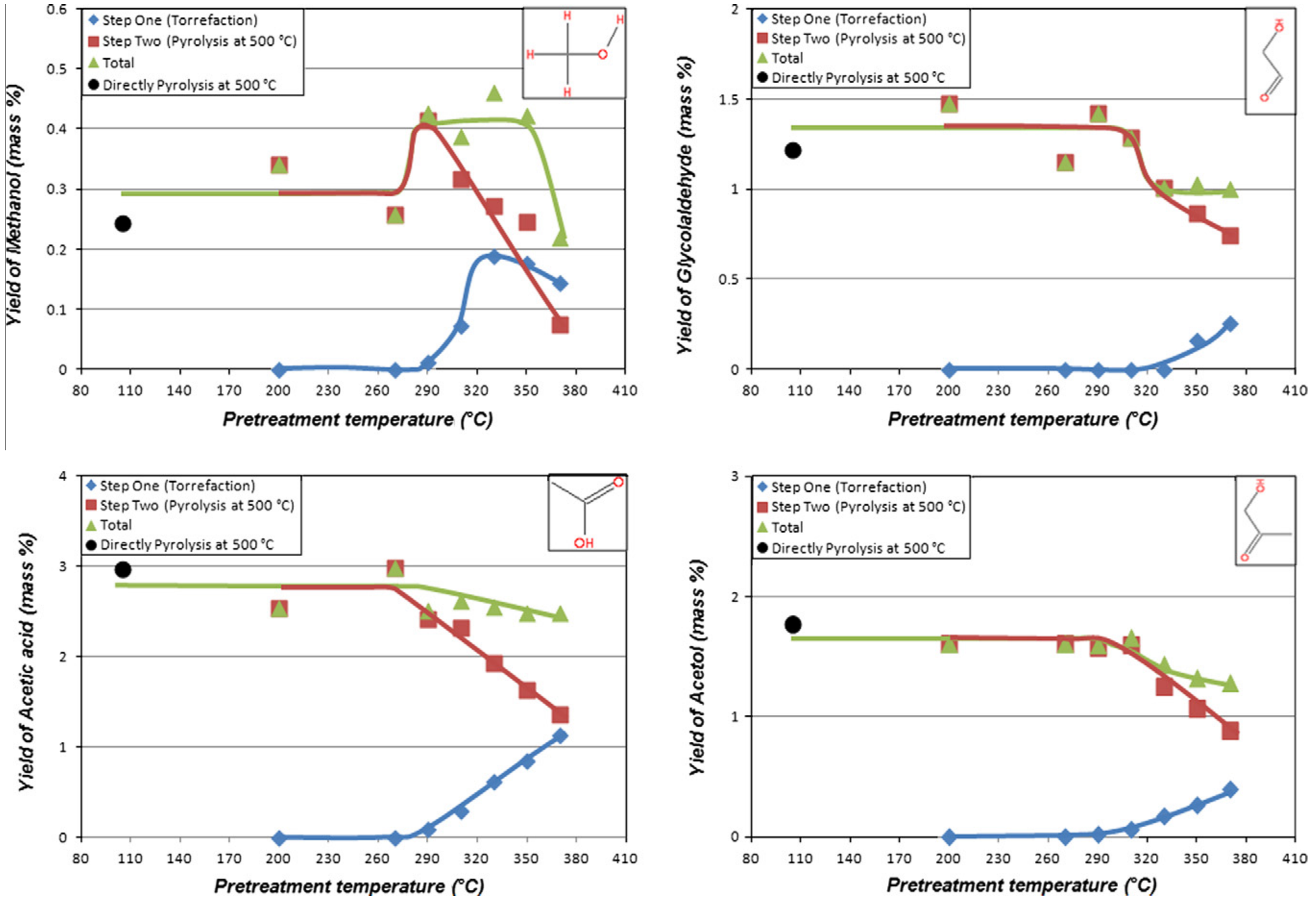

Fig. 7. Effect of pretreatment temperature on the yield of light compounds in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

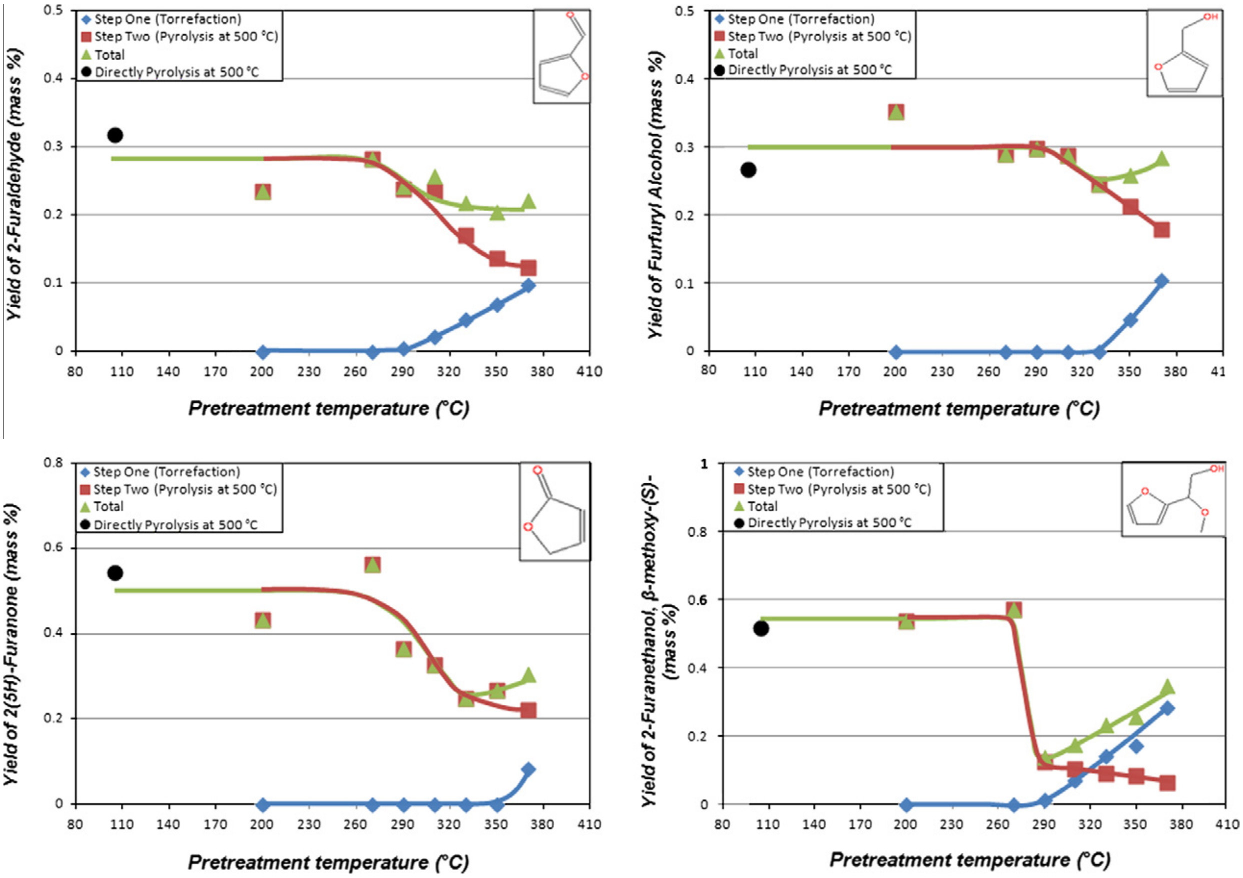

Fig. 8. Effect of pretreatment temperature on the yield of furanic compounds in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

Fig. 3 shows the yield of cellulose (as glucose), hemicelluloses (calculated as the addition of the yield of arabinose, galactose and mann/xylose), lignin and extractives. These yields were obtained by multiplying the content of each of the fractions shown in Table 1 by the yield of the solid residue reported in Fig. 2a. Clearly, most of the weight losses observed during pretreatment are due to the removal of hemicellulose and cellulose (likely the amorphous part of cellulose). No major changes were observed for the lignin and extractives. The fraction of hemicelluloses sharply decreases by more than 50% (from 19 mass% to 7 mass%). The decrease in the yield of cellulose (almost 25%) can be explained by the reduction of amorphous cellulose. Cellulose is a homopolysaccharide composed of β-D-glucopyranose units and the linear chains linked together by (1 → 4)-glycosidic bonds with an average degree of polymerization from 8000 to 10,000 [38,39] in amorphous and crystalline regions. The amorphous regions degrade more easily. The experimental results shown in Fig. 3 are in qualitative agreement with those published by Bridgeman et al. [40].

3.3. Thermogravimetric analyses

The DTG curves of Douglas-fir samples treated at different temperatures are shown in Fig. 4. This figure clearly show a reduction in the shoulder associated to the hemicelluloses confirming the compositional analyses reported in the previous section. At 370 °C most of the hemicellulose has been removed.

3.4. Karl-Fisher titration and yield of organic compounds

Fig. 5 shows the yield of water obtained in the thermal pretreatment step and in the pyrolysis step separately and when added. The overall yield of water increases as the torrefaction temperature increases and reaching a plateau of around 12–14 mass% at a torrefaction temperature between of 300 °C. Water could be formed from dehydratation of cellulose and hemicellulose [40–43]. It is interesting to note that most of the dehydratation occurs at temperatures over 290 °C. At lower pretreatment temperatures very little water was formed. At this temperature some fractions (lignin or amorphous cellulose) may melt creating the conditions for the formation of ionic species that catalyze dehydration reactions [44].

The content of organics in the bio-oil is calculated by subtracting the water yield from the total oil yield. The effect of pyrolysis temperature on the yield of organics is shown in Fig. 6. The yield of organics decreases gradually as the torrefaction temperature increases but is amplified at pretreatment temperatures over 300 °C. This could be due to the acceleration of dehydratation and polycondensation reactions leading to the formation of extra char, water, and gases as displayed in Fig. 2.

3.5. GC/MS and GC-FID

The yields of small C1–C4 molecules (methanol, glycolaldehyde, acetic acid, and acetol) on a biomass dry basis are presented in

Fig. 7 as a function of pretreatment temperature for the thermal pretreatment step, the pyrolysis step, and their addition.

At pretreatment temperatures above 290 °C, the yields of glycolaldehyde, acetic acid and acetol increase. Around the same pretreatment temperature, the yields of methanol, glycolaldehyde, acetic acid and acetol decrease during the pyrolysis step. In the case of methanol it is interesting to note that its yield increases at temperatures over 290 °C, plateaus at 320 °C and then decrease. The thermal pretreatment seems to enhance the production of methanol in the range of temperature between 290 and 350 °C. Methanol is produced from lignin methoxyl groups [16,17]. The increase in the yield of methanol indicates the acceleration of reactions involving the polycondensation of lignin during thermal pretreatment. The yield of glycolaldehyde, acetol and acetic acid do not seem to be affected by thermal pretreatment below 300 °C. Acetic acid is a product derived mostly from acetylated groups in hemicelluloses formed primarily from the initial elimination of the acetyl groups linked to the xylan chain on the C-2 position (glucomannan) [45] and from cellulose fragmentation reactions [46]. Glycoaldhyde and acetol are products from cellulose fragmentation reactions [38,39]. The reduction in the yield of these small oxygenated molecules could be caused by the enhanced dehydratation of cellulose temperature range which leads to the formation of dehydratated sugars less conductive to the formation of these compounds.

Fig. 8 shows the effect of pretreatment temperature on the yield of four furanic compounds (2-furaldehyde, furanyl alcohol, 2(5H)-furanone, 2-furanethanol, β-methoxy-(S)-). The yields of all these compounds are not affected by pretreated at temperatures below 290 °C. At higher temperatures their yields decrease, but increase again at still higher temperatures perhaps due to the acceleration of dehydration reactions at higher temperatures or the reduction of secondary reactions when these thermally unstable compounds are collected under lower reaction temperatures. Furanic compounds are formed from carbohydrates (cellulose and hemicelluloses) by a dehydration reaction during fast pyrolysis [35,47].

Table 2 and Fig. 9 show the effect of pretreatment temperature on the yield of phenolic compounds derived from lignin. Table 2 shows that the pretreatment temperature does not affect the yield of cresols and 3,4 dimethyl phenol, pyrocatechol and phenol, 2,4 (5)-dymethyl but heating at temperatures over 270 °C does affect the yield of phenol and phenol 4-methyl.

Pretreatment temperature affects dramatically the yield of the phenol with methoxyl groups but does not have much effect on the phenol with aliphatic chains. Fig. 9 clearly shows an important effect of pretreatment at temperatures over 270–290 °C on the yield of compounds derived from G units. The drastic decrease in the yield of these compounds could explain the increase observed in the yield of methanol in the same range of temperature (see Fig. 7). The increase in yield of eugenol, phenol, 2-methoxy-4-(propenyl)(E) and phenol, 2-methoxy-4-methyl at thermal pretreatments over 320 °C could be explained by the reduction of secondary reactions in the gas phase responsible for the formation of secondary products when these compounds are produced at lower temperatures (pretreatment temperature vs. pyrolysis temperature). These compounds are known to be susceptible to secondary reactions when produced at higher temperatures [48–50]. This also explains the reduction observed in the yield of methanol in the same range of temperature (see Fig. 7).

The drastic reduction in the yield of lignin derived compounds from G units when the biomass is pretreated at temperatures over 270 °C can be explained by the capacity of methoxyl groups to donate electrons. The importance of methoxyl groups on the formation of carbonaceous materials was highlighted by Hosoya et al. [51]. The authors found that the methoxyl groups are needed to form o-quinone methide intermediates for bio-char formation. This mechanism of bio-char formation implies the formation of 1,2-aryl migration products that are then converted to o-quinone methide by a dehydration reaction [51]. The formation of liquid intermediates when the Douglas-fir is heated at temperatures over 270 °C can accelerate the dehydratation reactions due to the formation of ionic species [44] and in this way accelerate the formation of o-quinone methide and the production of extra-char. The formation of liquid intermediates during biomass pyrolysis has been confirmed by Hass et al [52,53].

Table 2
Yield of some products derived from lignin.

Compound	Pretreatment temperature (°C)	Yield in pretreatment step (mass %)	Yield in pyrolysis step (mass %)	Total yield (mass %)
Phenol	200	0.000	0.282	0.282
	270	0.000	0.252	0.252
	290	0.003	0.217	0.220
	310	0.007	0.233	0.240
	330	0.016	0.219	0.235
	350	0.027	0.204	0.231
	370	0.041	0.169	0.210
O-Cresol	200	0.000	0.047	0.047
	270	0.000	0.028	0.028
	290	0.000	0.034	0.034
	310	0.000	0.045	0.045
	330	0.000	0.044	0.044
	350	0.000	0.039	0.039
	370	0.002	0.032	0.033
ρ-Cresol and μ-Cresol	200	0.000	0.101	0.101
	270	0.000	0.072	0.072
	290	0.000	0.071	0.071
	310	0.000	0.085	0.085
	330	0.000	0.079	0.079
	350	0.002	0.076	0.078
	370	0.006	0.062	0.068
Phenol, 2,4-dimethyl- and Phenol, 2,5-dimethyl-	200	0.000	0.086	0.086
	270	0.000	0.046	0.046
	290	0.000	0.063	0.063
	310	0.000	0.089	0.089
	330	0.000	0.086	0.086
	350	0.000	0.069	0.069
	370	0.002	0.056	0.059
Phenol, 4-ethyl-	200	0.000	0.027	0.027
	270	0.000	0.024	0.024
	290	0.000	0.022	0.022
	310	0.000	0.026	0.026
	330	0.000	0.023	0.023
	350	0.000	0.020	0.020
	370	0.000	0.017	0.017
Phenol, 3,4-dimethyl-	200	0.000	0.031	0.031
	270	0.000	0.013	0.013
	290	0.000	0.020	0.020
	310	0.000	0.025	0.025
	330	0.000	0.024	0.024
	350	0.000	0.021	0.021
	370	0.000	0.017	0.017
Pyrocatechol	200	0.000	0.477	0.477
	270	0.000	0.423	0.423
	290	0.000	0.349	0.349
	310	0.000	0.430	0.430
	330	0.000	0.457	0.457
	350	0.000	0.411	0.411
	370	0.077	0.334	0.411

3.6. Yield of lignin derived oligomers

The effect of pretreatment temperature on the yields of pyrolytic lignin is presented in Fig. 10. The total yield of both the water

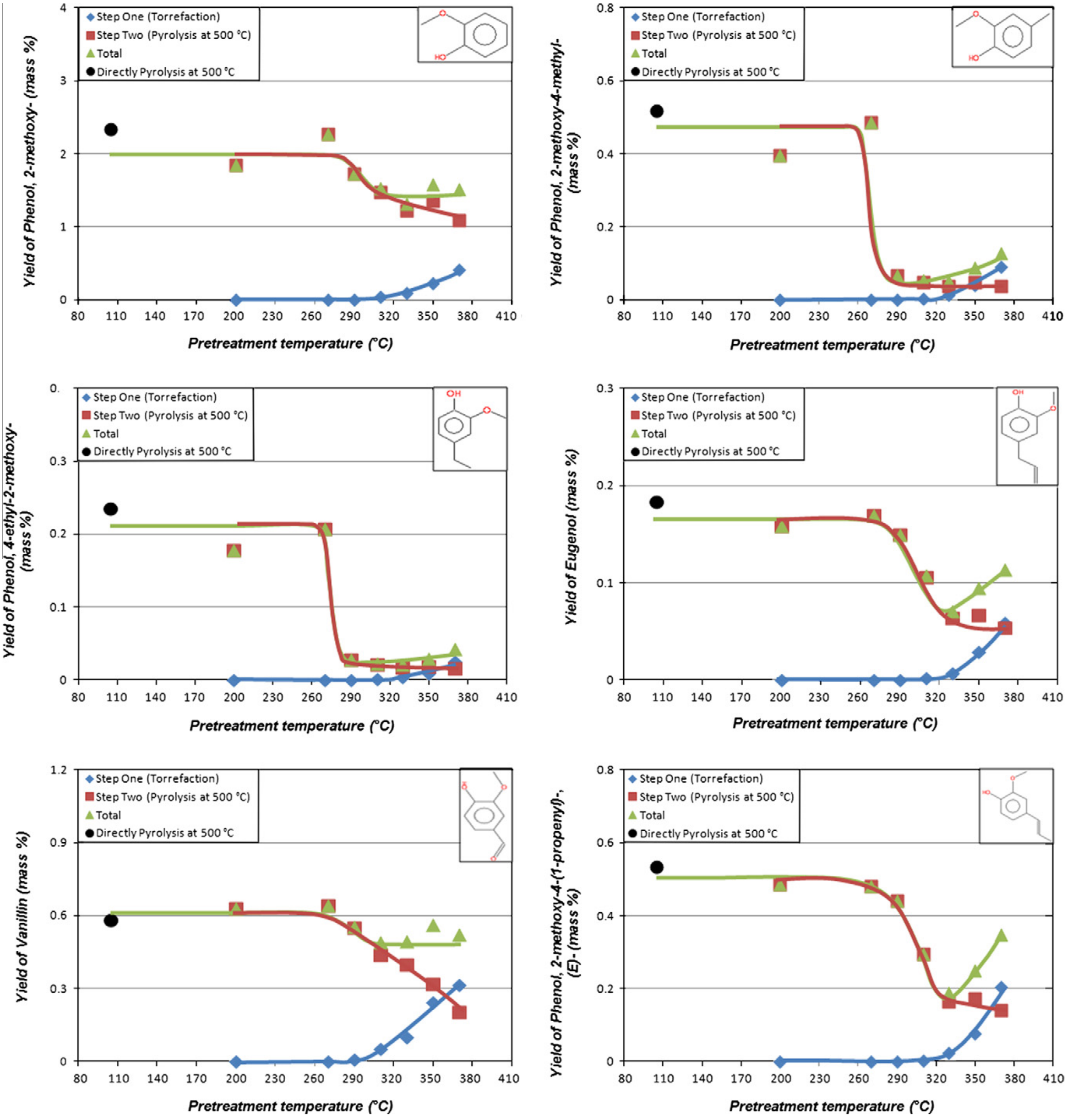

Fig. 9. Effect of pretreatment temperature on the yield of phenolic compounds (Group 3) in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

insoluble – CH_2Cl_2 soluble fraction (low molecular weight pyrolytic lignin) and the water – CH_2Cl_2 insoluble compounds (heavy pyrolytic lignin) gradually decrease as the thermal pretreatment temperature increases.

3.7. Sugar analysis (IEC-ion exchange chromatography) and GC/MS

Fig. 11 shows the effect of thermal pretreatment temperature on the yield of levoglucosan. Thermal pretreatment does not seem to affect the yield of this anhydrosugar for temperatures below 270 °C. Yields of around 4 mass% are obtained for fresh biomass and when the sample was pretreated at temperatures below 270 °C. At higher pretreatment temperatures the dehydratation and cross-linking reaction of cellulose may lead to the formation of dehydrated cross-linked sugars [41,43].

The effect of pyrolysis temperature on the yield of sugars (glucose, arabinose, galactose, fructose, mannose and xylose) produced when the aqueous phase obtained after lignin precipitation was hydrolyzed with sulfuric acid is shown in Fig. 12. The glucose reported was mostly derived from the levoglucosan and other oligo-anhydrosugars such as cellobiosan [54] found in bio-oils. The other 5-carbon sugars were derived mostly from the hemicellulose.

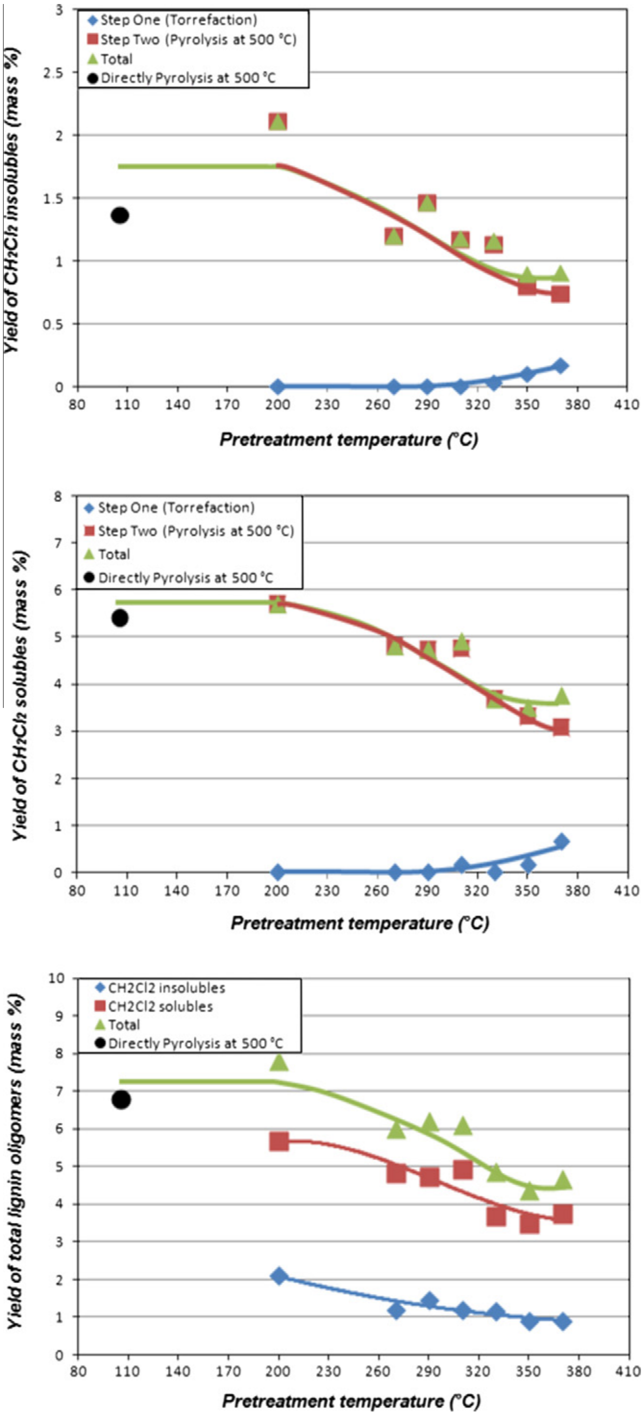

Fig. 10. Effect of pretreatment temperature on the yield of lignin oligomers in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

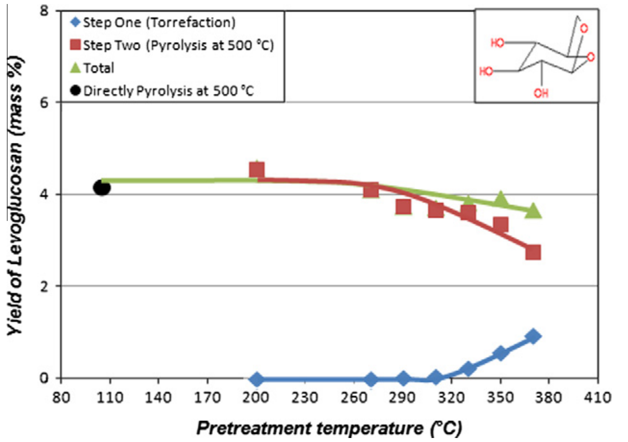

Fig. 11. Effect of pretreatment temperature on the yield of levoglucosan in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

The yield of glucose (a product of levoglucosan and oligo-anhydrosugar hydrolysis) and mannose and xylose decreased when the biomass was heated at temperatures as low as 200 °C. This may be an indication of the susceptibility of amorphous cellulose and xylan to thermal pretreatment. The yield of arabinose, galactose and fructose started to decrease at higher pretreatment temperatures, indicating the higher resistance of these sugars to thermal degradation and dehydratation. It is noteworthy that the overall yield of glucose, galactose and annose/xylose increases again when the pretreatment temperature exceeded 300 °C mostly due to the increase in the production of these sugars in the pretreatment step, which otherwise would be converted into non-sugar products during pyrolysis in a single step at 500 °C. Producing more sugars in the pretreatment step could mitigate primary fragmentation and secondary homogeneous reactions in the gas and solid phases compared with those that will be observed if these sugars were produced in a single step at 500 °C.

3.8. TGA of bio-oils

All the liquids produced in the pretreatment and pyrolysis steps were subjected to thermogravimetric analyses under nitrogen at a heating rate of 10 °C/min. The solid residue obtained was measured and multiplied by their yields. The results are shown in Fig. 13. The yield of solid residue (fixed carbon) in the liquids obtained was not affected for thermal pretreatment temperatures below 270 °C but decreases for higher temperatures to reach a plateau at pretreatment temperatures over 300 °C. These solid residues are mostly produced from the sugars and lignin oligomeric fractions. The shape of the solid residue curve is very similar to the one shown in Figs. 10 and 12 for the heavy fractions (lignin oligomers and sugars) responsible for most of the solid residue formed.

4. Conclusion

The effect of pre treatment temperature on the yield and composition of bio-oils derived from the auger pyrolysis of Douglas-fir was studied. Thermal pretreatment at temperatures below 270 °C does not seem to dramatically affect any of the biomass fractions. As the pretreatment temperature increases, the yield of water increases gradually plateaus at temperatures over 300 °C. The yield of lignin derived monomers with methoxyl groups (derived from G units) seems to be decreased dramatically and the yield of methanol increases when the biomass is heated at temperatures over 300 °C. The yield of lignin oligomers also decreases. The increase in the yield of water and methanol and the decrease in the yield of G derived monomers at temperatures close to 290 °C can be explained by the formation of liquid intermediates that provide the conditions for the formation of ionic species enhancing

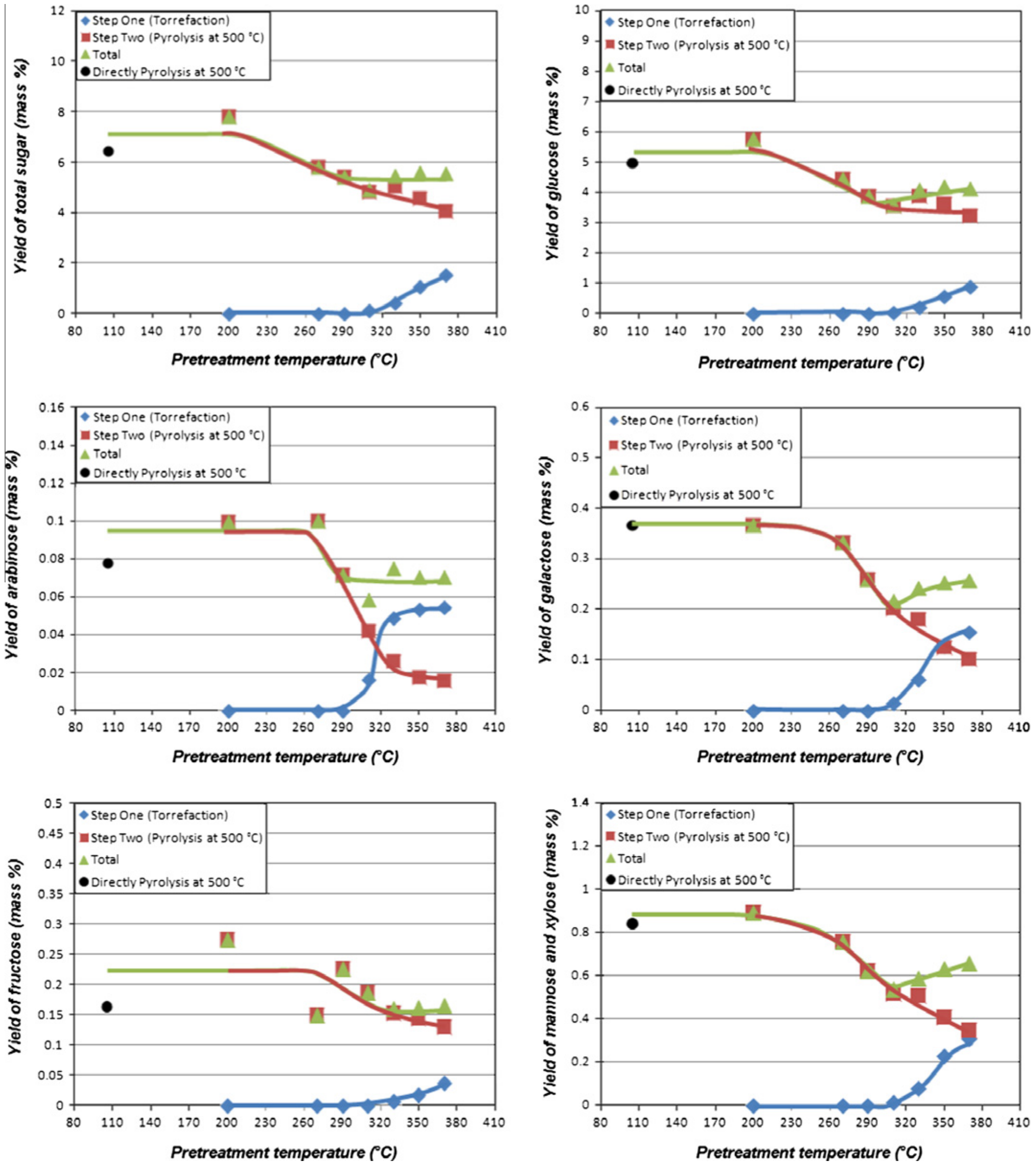

Fig. 12. Effect of pretreatment temperature on the yield of sugars in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

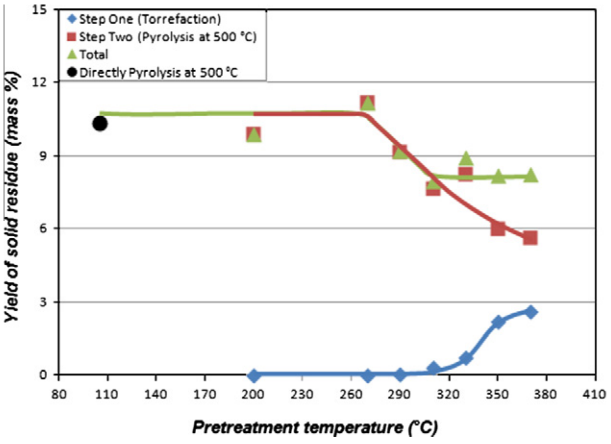

Fig. 13. Effect of pretreatment temperature on the yield of solid residue in the original biomass from auger pyrolysis of Douglas-fir wood with yields normalized per gram of dry initial biomass.

dehydratation reactions. These reactions seem to cultivate o-quinone methide intermediates critical for bio-char formation.

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